REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

0297

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TY. . AND DATES COVERED
	23 Aug 02	FINAL REPORT 01 MAR 01 TO 28 FEB 02

4. TITLE AND SUBTITLE
(DURIP-01) MULTI-DIMENSIONAL ULTRAFAST INFRARED VIBRATIONAL COHERENCE SPECTROMETER

5. FUNDING NUMBERS
F49620-01-1-0236
61103D
3484/US

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AFOSRNL
801 N Randolph Street, Room 732
Arlington, VA 22203-1977

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approve for Public Release; Distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer has been constructed. The instrument can be divided into four subsections: 1. generation of ultrashort visibe pulses, 2. generation of infrared (IR) pulses, 3. multiple IR beam propagation and sample excitation, 4. signal detection and processing. The figure shows a schematic of the instrument.

20021015 061

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclass	Unclass	Unclass	

REPORT: Grant Number: F49620-01-1-0236

PRINCIPAL INVESTIGATOR: Professor Michael D. Fayer

INSTITUTION: Department of Chemistry, Stanford University

GRANT TITLE: Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer

AWARD PERIOD: 3/1/2001 - 2/28/2000 (Total funding period)

OBJECTIVES: To plan, develop, and construct an ultrafast infrared multi-dimensional vibrational coherence spectrometer. The spectrometer should be useable throughout wide ranges of the vibrational IR spectrum, and it should be capable of performing the world's fastest multi-dimensional IR coherence experiments.

APPROACH:

A multi-dimensional ultrafast infrared vibrational coherence spectrometer was developed for application to the spectroscopy of high-density polyatomic gases, for example, hydrocarbons, and other systems. The instrument has applications as a new analytical tool and for the study of vibrational interactions and dynamics that influence energy flow and chemical reactivity. The instrument is based on extensions of ultrafast vibrational echo techniques recently developed by the author. The instrument is capable of two types of 2D vibrational echo spectroscopies will be pursued: two-time methods and time-frequency methods. For two-time 2D experiments, three of the pulses are used to create the vibrational echo from the vibrational lines contained within the pulse bandwidth (~500 cm^{-1}). The fourth pulse is used to heterodyne detect the echo signal. The heterodyne signal is frequency resolved. A two-dimensional Fourier transform of the data yields a 2D vibrational echo spectrum. The spectrum provides information on

vibrational interactions and can be used to help assign vibrational peaks in a complex spectrum of a mixture of molecules. To obtain the 2D time-frequency spectrum, the echo pulse is directed into a scanning monochromator, and its spectrum is taken as a function of the delay between pulses 1 and 2. The resulting spectra can extract information not available from vibrational absorption and other vibrational spectroscopic methods. As part of their technical education, graduate students and postdoctoral students developed the instrument and are now applying it to research.

ACCOMPLISHMENTS:

The Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer has been constructed. The instrument can be divided into four subsections: 1. generation of ultrashort visible pulses, 2. generation of infrared (IR) pulses, 3. multiple IR beam propagation and sample excitation, 4. signal detection and processing. The figure shows a schematic of the instrument.

1. Generation of Ultrashort Visible Pulses

Ultrashort pulses are generated using Ti:Sapphire laser technology. The world's shortest high power pulses using regenerative amplifier have been produced by combining and modify commercial equipment. A Nd:Vanadate diode pumped intracavity double laser (Spectra Physics) produces 4 W of green light to pump a Ti:Sapphire oscillator (K&M Lasers). The oscillator produces pulses with bandwidth always in excess of 55 nm centered at 800 nm. The output of the oscillator is directed through a telescope to modify the beam size, and the resulting beam is directed into a regenerative amplifier (regen). This beam serves as the seed for the regen. The regen is pumped by the output from a Q-switched, intracavity doubled Nd:YLF laser

(Quantronix). 7 W of 527 nm light measured at the Ti:Sapphire regen rod is used to pump. The regen (Spectra Physics) has been modified to produce ultrashort output pulses. (See technology Transfer below). The duration of the resulting pulses are measured with a real time autocorrelator (Spectra Physics). The pulses are 26 fs with a stability of 1/2 %. The duration and stability are each a factor of two improvement over the Spectra Physics specifications. The pulses are output from the regen at 1 kHz repetition rate and have an energy of 2/3 mJ per pulse. This portion of the system is shown in the upper left and middle part of the figure.

2. Generation of Infrared Pulses

The output of the regen is directed into a optical parametric amplifier (OPA) (Spectra Physics) that has been substantially modified. (See Technology Transfer below.) The input Ti:Sapphire pulses are split into three beams in the OPA. A weak beam generates a "continuum" in sapphire. The continuum is directed into a 2 mm long piece of BBO Type II crystal along with another portion of the Ti:Sapphire pump beam. The near IR wavelength at ~1.3 μm is amplified by optical parametric application to produce amplified 1.3 μm (signal) and ~2 μm (idler) collinear beams. The signal is discarded, and the idler is redirected into the BBO along with the main portion of the Ti:Sapphire pump beam. The output of the second pass of the BBO is ~60 μJ of combined signal and idler. Because the differences in the index of refraction, the signal and idler are not time coincident. The beams go through a retiming system. The time coincident signal and idler pass through a telescope and are incident on a 0.5 mm $AgGaS_2$ crystal. This crystal produces the mid-IR difference frequency of the signal and idler. The frequency is tuned by tuning the frequencies of the signal and idler, which is

accomplished by changing the phase matching angle of the BBO crystal. The mid-IR output of the OPA is directed into

the multiple IR beam propagation and sample excitation system.

3. Multiple IR Beam Propagation and Sample Excitation system

The main portion of the figure shows the multiple beam paths that combine to make the necessary input IR laser pulses for the experiments. Four beams are shown. There is actually a fourth beam, called the tracer beam that passes through the sample along the same path as the vibrational echo signal. The three beams that are called excitation pulses generate the vibrational echo signal. The timing of these beams must be controlled extremely precisely. It is necessary to control reproducibly the timing of the pulses to ~0.5 fs. This requires state of the art position equipment because of the need for reproducibility that is better than 1/20 of a wavelength of light. The time of the beams are controlled by three linear motor ultra precision translation stages (Aerotech). The nonlinear interaction of the three excitation pulses with the sample produces the vibrational echo pulse that emerges from the sample. This pulse is overlapped in space and time with the heterodyne detect pulse, and the pair of pulses are directed into a monochromator.

4. Signal Detection and Processing

The combined vibrational echo and heterodyne pulse are directed into a monochromator (middle left on the figure). The monochromator disperses the incoming beams into their component wavelengths. The signal is detected by an 32 element liquid nitrogen cooled MCT IR array detector (Infrared Systems Development/Infrared Associates). The 32 element array detector makes it possible to measure 32 to

wavelengths at once. The monochromator is under computer control. With the monochromator at a single wavelength, the times are scanned. The monochromator is then moved to a new wavelength, and time dependent data at 32 new wavelengths are collected. The array detector, which was in part developed in the course of this project (see Technology Transfer below), makes data collection 32 times faster than using a single element detector. The data from the array is read out by computer to give data as a function of time and wavelength.

The development and construction of the Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer is complete. Experiments have recently begun utilizing the instrument. The ongoing research is support by AFOSR under grant # F49620-01-1-0018.

PUBLICATIONS:

There are no publications because this was an equipment grant. The construction of the instrument took somewhat longer than the grant. We are currently conduction experiments with the instrument under AFOSR support (grant # F49620-01-1-0018).

DISCLOSURES AND PATENTS:

None

TECHNOLOGY TRANSFER:

In the course of developing the Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer, substantial technology transfer occurred to the companies that provided various components of the equipment. Many of the components are state of the art. The Fayer laboratory modified and perfected the equipment working in conjunction

with the companies. In addition, the Fayer lab provided a great deal of test information that was not possible for the companies to measure themselves.

1. Spectra Physics Ultrafast Regenerative Amplifier. The system that Spectra Physics solid specified a pulse duration of 50 fs. Through detailed analysis of the regen, we were able to make modifications that brought the pulse duration down to 26 fs as measured by the technical staff of Spectra Physics. The most important modification was the pulse stretcher. By modifying a particular component, it was possible to have a much larger and more collimated beam enter the stretcher. In the original factory configuration, the beam could not be collimated over the length of the stretcher. Following the modification, the beam could be collimated over a distance that is twice the length of the stretcher. This resulted in improved characteristics in the stretcher and the resulting much shorter pulses. Spectra Physics has now incorporated the Fayer lab modifications into the product that they are selling.

2. Spectra Physics Ultrafast Optical Parametric Amplifier. As delivered, the Spectra Physics ultrafast OPA was untested. It was delivered under an agreement that the Fayer lab would perfect the device and feed back the results to Spectra Physics. A substantial number of improvements were made to the Spectra Physics standard version of the OPA. A rotation stage was added to the half wave plate that controls the intensity of light use to generate the continuum (see above). The improved control proved very important. The timing translation stages that control the timing of the Ti:Sapphire input pulses were modified to use differential micrometers that could be adjusted from outside of the OPA box. The accurate control of the pulse timing is essential for making ultrashort IR pulses. A section was added to the OPA to separate, retime, and recombine the signal and idler

beams (see above). This is essential to have the signal and idler overlapped in time when they enter the final $AgGaS_2$ crystal that generates the IR. A telescope was added to properly size and collimate the signal and idler going into the $AgGaS_2$ crystal. All of these modification lead to the production of the world's shortest IR pulses, that is, 40 fs.

3. Infrared Systems Development/Infrared Associates 32 Element MCT IR Array Detector. A great deal of work was done with Infrared Systems Development/Infrared Associates to perfect both the array and the associated electronic. As delivered the array and electronics were incapable of performing the function that they were designed to perform. Infrared Systems Development and Infrared Associates are to separate but linked companies. Infrared Associates manufactures the array, which is composed of 32 MCT detectors on a chip with the necessary connections to provide power and bring out signals. It is housed in an evacuated liquid nitrogen Dewar. The array is powered and read out by electronics produced by Infrared Systems Development. The readout is complex. The 32 elements are followed by 32 matched amplifiers and 32 gated integrators. The signals from the 32 gated integrators are read by a multiplexed analog to digital computer, and the information is transferred to computer. Neither of these companies had the capability of testing their products under actual conditions of use. Following measurements made in the Fayer lab, the device was returned to the manufactures for modification. Several rounds of testing by the Fayer lab and changes by the companies took place. Both the chip and the electronics required substantial revisions. The changes that were instituted as a result of the testing by the Fayer lab have now been incorporated into the current production of the devices.

Multi-Dimensional Ultrafast Infrared Vibrational Coherence Spectrometer